

## PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

## Activated Azodicarbonamide

We, NATIONAL POLYCHEMICALS, INC., a Corporation organized and existing under the laws of the Commonwealth of Massachusetts, of Eames Street, Wilmington, Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an azodicarbonamide composition.

The selection of a suitable chemical blowing agent for forming a cellular and foamed plastic or synthetic resin is commonly made with reference to the temperature at which the blowing agent decomposes to evolve gas and to the fluidity temperature range of the plastic to be blown. Azodicarbonamide has a decomposition temperature in air of about 195° to 200° C and about 190° C in dioctyl phthalate. For many applications it is desirable that azodicarbonamide should decompose at a much lower temperature. Decomposition at a lower temperature would permit a reduction in the thermal degradation of the plastic composition in which azodicarbonamide is incorporated as a chemical blowing agent. Furthermore, lower decomposition temperatures would permit shorter processing cycles and allow enhanced decomposition rates, thereby permitting lower processing temperatures or shorter residence times or a combination thereof.

It is now known that some heavy metal compounds have an activating effect on chemical blowing agents in the sense that they tend to lower the temperature at which the blowing agent decomposes with evolution of gas. However, even the most active heavy metal compound fails to lower the decomposition temperature of azodicarbonamide below about 160° C. For example, dibasic

lead phosphite lowers the decomposition temperature of azodicarbonamide in a typical plastisol composition to about 170° C.

It is an object of the invention to provide a composition which will substantially lower the decomposition temperature of azodicarbonamide and/or to provide an activated azodicarbonamide composition which has an enhanced decomposition rate.

It has been found that the decomposition temperature of azodicarbonamide is substantially lowered, for example to below 160° C, by an activating composition comprising a mixture of a compound of a metal of Group II and/or Group IV of the Periodic Table and an alkali metal-containing compound. It has also been found that the employment of very finely divided azodicarbonamide having an average particle size of about 2.8 microns, or less, in combination with the activating composition further lowers the decomposition temperature of the azodicarbonamide to about 140° C or below. Additionally, the activating composition also promotes the heat and light stability of the plastic composition in which it is incorporated. This reduction in decomposition temperature is quite unexpected in that the mixtures of metals of Group IV and alkaline earth metals, or mixtures of alkaline earth metals themselves fail to produce similar results.

The Group II and Group IV metals comprise polyvalent metals, and include metals of Group II, such as calcium, strontium and barium and particularly magnesium and the Group IIb metals such as zinc, cadmium and mercury and metals of Group IV such as titanium, tin and lead and combinations of Group II and Group IV metals. The alkali metals of the composition include those monovalent metals of Group I of the Periodic Table, and particularly Group Ia, such as

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sodium, potassium, lithium, caesium and combinations thereof.

The metal- and alkali metal-containing compounds of the compositions may be employed as organic or inorganic compounds or combinations thereof. For example, inorganic compounds may include compounds such as oxides and salts such as carbonates, phosphites, halides and phosphates. Suitable specific compounds include zinc oxide, lead carbonate, potassium chloride and lead dibasic phosphite. However, the use of compounds containing organic radicals is generally recommended for use with plastic compositions to promote solubility of the compounds in the organic plastic compositions. Suitable organic radicals comprise aromatic, aliphatic, alicyclic, heterocyclic and alkylene groups. For example, suitable aliphatic radicals include: short and long chain fatty acids such as tallates, oleates, acetates, propionates, 2-ethylhexoates, ricinoleates, myristates, octoates, stearates and resin soaps (resinates) and mixtures thereof; alicyclic radicals include naphthenes; aromatic radicals include phthalates, phenates and benzoates, as well as other radicals such as mercaptides, etc.

The metal and alkali metal-containing compounds of our compositions are often formed by the reaction of the metal or a metal salt with an organic acid such as mono- or poly-carboxylic acid or its derivatives to form the corresponding metal salt or metal soap. Alkali metal soaps of long chain fatty acids of more than 6 carbon atoms together with heavy metal containing soaps of from 2 to 12 carbon atoms have been found to be an excellent combination for use in vinyl resin compositions.

Granulate azodicarbonamide is decomposed in the presence of the activating decomposition at very low temperatures. When very finely divided azodicarbonamide is employed in combination with the activating composition, even lower decomposition temperatures may be obtained. For example, it has been found that azodicarbonamide precipitated, or ground to a particle size range of from 0.1 to 5 microns with an average particle size range of about 2.8 microns, e.g. 2.0 to 1.8 microns, or less in combination with the activating compositions evolves gas at temperatures of 130 to 140° C or lower.

Activation of azodicarbonamide is achieved when the weight ratio of the alkali metal compound to the Group II and/or Group IV metal compound is from one to five to five to one with optimum results observed at a ratio about one to two. The activating composition of the invention is commonly employed in a weight ratio of activating composition to the blowing agent of from one to ten to four to one with good results obtained at a ratio of about one to two.

Accordingly the invention also provides a

method of enhancing the decomposition of azodicarbonamide which comprises contacting azodicarbonamide with an alkali metal compound and a compound of a metal of Group II and/or Group IV, in the above proportions, and heating the azodicarbonamide to a temperature of 160° C. or less.

The activated azodicarbonamide composition is incorporated in a plastic composition in a sufficient amount to effect the desired chemical blowing action. This amount may vary from 0.5 to 50 parts by weight of the activated azodicarbonamide composition to 100 parts by weight of the plastic or resin content of the fluid, plastic composition. In the atmosphere, or in open mould blowing operations, such as in blowing, or forming, blown, cellular plastic sheets or layers on a carrier sheet, from one to ten parts by weight per one hundred parts by weight of the resin are commonly employed. In closed moulds or pressure moulding operations higher amounts of from ten to fifty parts by weight per one hundred parts by weight of the resin are often used.

The Group II and/or Group IV metal compound, alkali metal compound and the azodicarbonamide may be premixed together or added separately, or in any combination, to the plastic composition. The desired Group II and/or Group IV metal and alkali metal concentration to obtain activation may be obtained from other ingredients added to the plastic composition for other purposes. For example, all, or part of, the Group II and/or a Group IV metal concentration may be obtained from Group II and/or Group IV metal phosphites, or soaps, or Group II and/or Group IV metal soaps added to the plastic composition as stabilisers. One method of preparing suitable compositions for use is to form a fluid slurry of the activating composition or the activated azodicarbonamide composition in an organic ester plasticiser or in a plasticiser-resin mixture.

The activated azodicarbonamide composition of the invention may be employed with a wide variety of plastic compositions to produce open or closed, cellular structures in block, sheet or in other form. The activated composition will find particular utility with those thermosetting and thermoplastic compositions which require lower decomposition temperatures than those normally obtained with azodicarbonamide, e.g. those having a fluid state below 190° C. Suitable gas-retentive and gas-expandable, organic polymeric plastic materials and compositions include but are not limited to: vinyl resins and vinyl resin compositions which may comprise a vinyl resin dispersed in a high boiling organic ester plasticiser which plasticiser solvates the resin at an elevated temperature to produce a fused, flexible vinyl resin; natural and synthetic elastomers such as natural rubber

and natural rubber latices; butyl and chloro-butyl rubbers, ethylene-propylene rubbers; vinyl-diene copolymers such as styrene-butadiene copolymers; nitrile rubbers such as acrylonitrile - diene copolymers; polydienes such as poly-butadienes; polyisoprenes; polychloroprene; silicones; epoxy resins; phenolic resins such as phenolformaldehyde resins; urea-aldehyde resins; polyolefins particularly low melting point, branch chain polyethylene and polypropylene; polyesters; alkyd resins; polystyrene; olefin polysulphides, polyethers; cellulosic esters and other resins; and mixtures and combinations thereof. These plastic compositions may be in latex, bulk emulsion or solution form. The vinyl resins are often employed in high boiling organic ester plasticisers of high boiling point, for example dialkyl and monoalkyl phthalates. Vinyl halide resins include polyvinyl chloride and copolymers of vinyl chloride with vinyl esters of short chain fatty acids such as vinyl acetate, vinyl propionate, as well as other vinyl halides such as vinylidene chloride and the like and copolymers with maleic acid esters and the like combinations thereof. These blowable, organic plastic materials are characterised by the feature that they are capable of setting to a normally solid state either by cooling or curing, in which latter case a suitable amount of curing agent is desirably present, and have sufficient consistency and tensile strength at temperatures of from about 80° C to 200° C or higher to retain the expanded structure resulting from the evolution of gas either in the mould or when removed therefrom.

The plastic materials in which the activated azodicarbonamide compositions of the invention are incorporated can be formed either before or after blowing by coating, slush moulding, compression or injection moulding, extrusion or combinations thereof. The foamed material can be retained in its cellular or foamed form by cooling in the case of

thermoplastic materials and by cooling and curing with curing agents or effecting cross linking in the case of thermosetting materials. The cellular material can be formed on sheets or substrates such as paper, canvas, cloth, plastic films, screens and the like and may find particular utility such as shoe soleing, gaskets, shock absorbing functions and the like.

The plastic materials may also contain other ingredients and additives to enhance other properties such as to promote processing or final product acceptance. These additional materials may include heat and light stabilisers, plasticisers, antioxidants, dispersing agents, wetting agents, lubricating agents, pigments, dyes, blending resins, curing agents and the like. These additives would include organic phosphorus compounds, epoxy compounds, low and high boiling ester-type plasticisers, low volatility polyols, fatty acids and fatty acid soaps, alkanol amines, amines, poly(alkylene polyamines) such as diethylene diamine and low molecular glycols and the like. These plastic materials may also include inert filler materials, such as clays, metal oxides, carbonates, whitenings, asbestos, glass fibres, wood flour, diatomaceous earth and the like in a ratio of from 20 to 300 parts of inert filler material to each hundred parts of resin.

The activated composition, or the like activated azodicarbonamide composition of the invention can be incorporated into the material by a number of methods. It may be added as a plasticiser slurry or in an organic solvent solution to the resin-plasticiser composition. It may be admixed with the solid resin or added directly to the resin during processing or by any method wherein the azodicarbonamide and the activating composition are combined and uniformly admixed in the plastic composition.

The invention is further illustrated by the following detail of examples:

## EXAMPLE 1

A vinyl resin ester plasticising dispersion composition was prepared of the following ingredients:

Ingredients	Parts by Weight
*Vygen 161	70.0
*Vygen 85	30.0
Diocetyl phthalate	90.0
Epoxidized soybean oil	5.0
Pigments	6.5
Azodicarbonamide (average particle size less than about 3.0 microns)	4.0
	205.5

\* Essentially a polyvinyl chloride resin of varying molecular weight manufactured by the General Tire Co.

The additives listed in Table 1, singly in separate experiments, were then thoroughly dispersed and incorporated into the above composition and a thin layer of the resulting formulation was heated under atmospheric conditions to a temperature of about 203° C for 50 seconds and cooled. The thickness of the foamed resin sheet obtained was measured with a Randall-Stickney thickness gauge and from this measurement and the surface area and the weight of the sheet the apparent density of the foamed sheet was calculated. The density data obtained with each additive composition are given in Table 1.

TABLE 1

Additive	Parts of Additive per 100 parts of vinyl resin	Apparent Density lbs./cu. ft.
1. —	—	72
2. Zinc oxide	3.0	72
3. Barium myristate	3.0	72
4. Zinc oxide and barium myristate	3.0 3.0	64.5
5. Potassium oleate Barium myristate	5.2 3.0	54
6. Potassium Oleate Barium myristate Zinc oxide	5.2 3.0 3.0	19.25

The resulting data demonstrate a wide difference in vinyl foam density at similar air temperatures and residence times indicating a lowering of the decomposition temperature of the blowing agent by the activating effect of some of the additives. The use of Group II additives alone, such as zinc oxide, or the oil-soluble barium soap, gave little if any change in foam density.

- 5 The use of the barium soap and zinc oxide together gave a small reduction of about six lbs. per cubic foot in density. The use of an alkali metal compound and an alkaline earth metal compound together, namely the potassium and barium soaps, gave a reduction in foam density of about 18 lbs. per cubic foot. The employment of a combination of a heavy metal of Group IIb such as zinc, with the alkali metal potassium produced a fully unexpected activating effect and gave a reduction in foam density of over 52 lbs. per cubic foot. This example illustrates that the apparent density of the foamed plastic composition can be substantially lowered by employing the activating admixture of an alkali metal and a heavy metal.

## EXAMPLE 2

An activated azodicarbonamide dispersion for the production of a chemically blown cellular vinyl composition was prepared as follows:—

## Activated Blowing Agent Dispersion

	Rate by Weight
Azodicarbonamide (average particle size of 14 microns or less)	165
Zinc 2-ethylhexoate (22% zinc content)	54
Potassium oleate (85% active)	25
Dioctyl phthalate	295.5
Dispersing agent such as a fatty acid amine or amide	2.5
	542.0

- 20 The potassium soap was dispersed in the ester plasticiser until a uniform dispersion was obtained, and the zinc compound added and blended to produce a uniform dispersion. The dispersing agent was then added followed by the finely divided azodicarbonamide which was added slowly with stirring until a uniform yellow slurry which poured readily at room temperature was obtained. This dispersion when incorporated into a plastic material for blowing purposes had a decomposition temperature of about 140° C or less. This dispersion also possesses a faster decomposition rate than a conventional azodicarbonamide with equivalent amount of either a dibasic lead phosphite, or a barium-cadmium-zinc soap additive.
- 25 The above dispersion was incorporated in the following formulation to provide a plastic material capable of being blown as follows:

## Vinyl Resin Formulation A

	Parts by Weight
*PVC No. 7402	100.00
Dioctyl phthalate	65.00
Butyl octyl phthalate	30.00
Flexol EPO (epoxidized soybean oil)	5.0
Titanium oxide	5.0
Activated blowing dispersion	6.1
	211.1

\* A homopolymer of polyvinyl chloride manufactured by Diamond Alkali Co.

A similar vinyl-ester plasticiser composition was prepared in a similar manner for comparison purposes and identified as formulation B. In B formulation the blowing agent dispersion contained azodicarbonamide having an average particle size of about 3.0 microns, and the potassium and zinc soaps were replaced by an equivalent amount of liquid vinyl stabiliser identified as Ferro 1720. (The word "Ferro" is a Registered Trade Mark). This stabiliser comprises a mixture of barium, cadmium and zinc compounds, such as barium phenate and cadmium and zinc 2-ethylhexoates.

The formulations A and B were thereafter evaluated in the degree of expansion as a function of temperature and residence time in an air oven with the results graphically illustrated in the accompanying drawings, in which

Figure 1 is a curve of the apparent density, a measure of the degree of expansion, plotted against the temperature, and

Figure 2 is a curve of the apparent density plotted against residence time.

From Figure 1, with a residence time in the air oven of  $1\frac{1}{2}$  minutes, it is seen that formulations A and B gave products which

varied considerably in foam density with temperature. Formulation B had an activated temperature at which the blowing agent decomposed to evolve gas of approximately 170 to 180° C, while the decomposition temperature of the azodicarbonamide in formulation A was about 150° C. Formulation A also gave foams having densities as low as 10 to 15 lbs. per cubic foot, while formulation B at similar temperatures gave foams having densities which were about twice those of formulation A. The superiority of the alkali metal-heavy metal combination over the alkaline earth mixture is thus readily apparent from these graphical data.

In Figure 2 the degree of expansion of each of formulations A and B is shown as a function of residence time, at a temperature of about 200° C. Formulation A is seen to be much superior to formulation B in providing a low density foam in a relatively short period of time. This ability to achieve low foam densities with a relatively short residence time is most desirable since it reduces thermal degradation of the polymeric materials, enhances production efficiency and improves processing rates.

### EXAMPLE 3

Suitable combinations of alkali metal-heavy metal compounds for activating purposes include but are not limited to the following admixtures:

I	dibasic lead phthalate sodium stearate
II	titanium octoate sodium phenate
III	cadmium naphthenate lithium hydroxy stearate
IV	barium naphthenate potassium tallate cadmium ricinoleate
V	magnesium oxide zinc oxide potassium lauryl sulphate
VI	tin mercaptide lithium carbonate potassium oleate
VII	titanium oxide zinc acetate potassium 2-ethylhexoate

The combination of a heavy metal and an alkali metal with or without very fine particle sized azodicarbonamide blowing agent per-

mits the use of lower decomposition temperatures and shorter residence time in preparing cellular plastic foam material.

## WHAT WE CLAIM IS:—

1. A composition comprising azodicarbonamide, an alkali metal compound and a compound of a metal of Group II and/or a Group IV of the Periodic Table in proportions such that decomposition of the azodicarbonamide occurs with evolution of gas when the composition is heated to a temperature which is not above 160° C.
2. A composition comprising azodicarbonamide, an alkali metal compound and a compound of a metal of Group II and/or Group IV, in which the weight ratio of the Group II and/or Group IV metal compound to the alkali metal compound is from five to one to one to five; and the ratio of the metal compound to azodicarbonamide is from one to ten to four to one.
3. A composition according to claim 2, in which the second compound is zinc oxide.
4. A composition according to any one of claims 1 to 3, in which the Group II and/or Group IV metal is present as the salt of a carboxylic acid.
5. A composition according to any one of the preceding claims, in which the alkali metal compound is a potassium compound.
6. A composition according to any one of the preceding claims, in which the alkali metal compound is a salt of a carboxylic acid.
7. A composition according to any one of the preceding claims, in which the azodicarbonamide has an average particle size of 2.8 microns or less and a particle size range of from 0.1 to 5.0 microns.
8. A composition according to any one of the preceding claims, in which the weight ratio of the Group II and/or Group IV metal compound to the alkali metal compound is substantially 2:1.
9. A composition according to any one of the preceding claims, in which the weight ratio of the metal compounds to azodicarbonamide is substantially 1:2.
10. A composition comprising azodicarbonamide and additive 5 or additive 6 of Example 1.
11. A composition comprising azodicarbonamide, zinc 2-ethylhexoate and potassium oleate as in Example 2.
12. A composition comprising azodicarbonamide and one of the admixtures I to VII of Example 3.
13. A composition according to any one of the preceding claims, in which the composition also contains a sufficient amount of an organic ester plasticiser to form a fluid slurry.
14. A mixture capable of being expanded in its fluid state by the decomposition of azodicarbonamide to form a cellular foam structure, which mixture comprises a major amount of an organic polymer having a fluid state below about 190° C and the composition claimed in any one of the preceding claims.
15. A mixture according to claim 14, in which the polymer is a thermosetting resin and the mixture contains a curing amount of a curing agent.
16. A mixture according to claim 14, in which the polymer is a thermoplastic material.
17. A mixture according to claim 16, in which the polymer is a vinyl resin and the composition contains an amount of a high boiling point organic ester plasticiser sufficient to solvate the vinyl resin at elevated temperatures.
18. A mixture according to any one of claims 14 to 17, in which the amount of azodicarbonamide is from 0.5 to 50 parts by weight per 100 parts by weight of the polymer.
19. A foamable resin composition comprising azodicarbonamide, an alkali metal compound and a compound of a metal of Group II and/or Group IV substantially as hereinbefore described with reference to any one of the Examples.
20. A composition comprising subdivided azodicarbonamide and an alkali metal compound in an amount sufficient to lower the decomposition temperature of azodicarbonamide to 160° C or lower when the composition is placed in contact with a Group II and/or Group IV metal-containing compound.
21. A method of enhancing the decomposition rate of azodicarbonamide, which comprises contacting azodicarbonamide with a compound of a metal of Group II and/or Group IV, and an alkali metal compound, the weight ratio of the Group II or Group IV metal compound to alkali metal compound being from five to one to one to five; and the weight ratio of the Group II or Group IV metal compound and alkali metal compound to azodicarbonamide being from one to ten to four to one; and heating the azodicarbonamide to a temperature of 160° C or less.

J. MURPHY,  
Agent for the Applicants.

